



TITLE:

Infrared Spectra and Molecular Configuration of Benzoic Acid (Special Issue on Physical Chemistry)

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CITATION:

Hayashi, Soichi ...[et al]. Infrared Spectra and Molecular Configuration of Benzoic Acid (Special Issue on Physical Chemistry). Bulletin of the Institute for Chemical Research, Kyoto University 1966, 44(4): 335-340

ISSUE DATE:

1966-10-31

URL:

<http://hdl.handle.net/2433/76131>

RIGHT:

Infrared Spectra and Molecular Configuration of Benzoic Acid

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Received August 16, 1966

Infrared spectra of benzoic and deuterobenzoic acids were measured at low temperatures. The characteristic bands of the COOH group near 1700, 1300 and 950 cm^{-1} were observed as pairs. This appears to indicate that two kinds of configurations having different energies and different spectra exist in the crystal. The energy difference was estimated to be about 0.1 Kcal./mole from measurements of intensity ratios of pairs at various temperatures. The nearly equal distances of the two C—O bonds in benzoic acid, *i.e.* 1.29 and 1.24 Å as determined by X-ray measurements, were interpreted as the average for the mixture of the two configurations.

INTRODUCTION

The crystal and molecular structures of benzoic acid were accurately determined by Sim, Robertson and Goodwin¹⁾, who reported that the molecules form nearly planar, centrosymmetrical dimers, with hydrogen bonds (2.64 Å) between adjacent carboxyl groups. They assigned the hydrogen atom of the carboxyl group to O₂, as shown in Figure 1 (A), though the resolution of this hydrogen atom was not good enough to confirm the assignment. This lack of resolution may indeed be connected with the nearly equal distances of the two C—O bonds, *i.e.* 1.29 and 1.24 Å, and indicate a ready transfer of hydrogen to the other oxygen across the

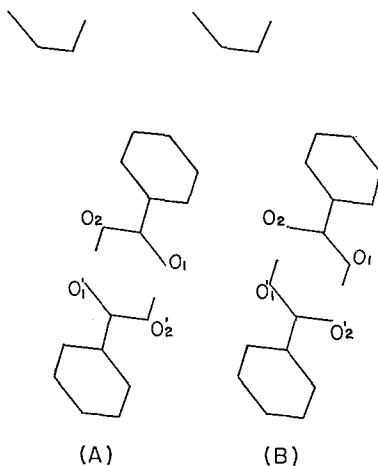


Fig. 1. Two kinds of configurations of benzoic acid.

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hydrogen bond.

If the two configurations of dimers of benzoic acid of Figure 1 are isolated, they must have the same energy and spectrum. However, when the dimers are in the crystalline potential field of C_i symmetry, they may have slightly different energies and show different spectra. In order to investigate these matters, the infrared spectra of benzoic and deuterobenzoic acids were measured at low temperatures.

EXPERIMENTAL

The benzoic acid supplied by the Tokyo Kasei Co. was further purified by recrystallization. The deuterobenzoic acid, C_6H_5COOD , was prepared by the recrystallization from aceton-deuterium oxide solution. Well oriented crystal layers of these samples were obtained by cooling the melts between two optically flat plates of rock-salt. Infrared spectra were measured by the Perkin Elmer 521 spectrometer, and the Koken DS-301 spectrometer equipped with two NaCl prisms and an AgCl polarizer.

RESULTS AND DISCUSSION

The infrared spectra of benzoic and deuterobenzoic acids measured at low temperatures are shown in Figures 2 and 3, respectively, and one of the polarized infrared spectra is shown in Figure 4.

1. Frequencies characteristic of the COOH and COOD groups

There are two bands at 1706 and 1684 cm^{-1} in the region of the stretching vibration of $\text{C}=\text{O}$ bonds of the dimeric units. The band at 1432 cm^{-1} or 1421 cm^{-1} at room temperature is due to one of the coupled vibrations of $\text{C}-\text{O}$ stretching and OH bending, the two bands at 1334 and 1298 cm^{-1} , or 1324 and 1288 cm^{-1} at room temperature, respectively, are in the region of another coupled vibration of $\text{C}-\text{O}$ stretching and OH bending, and those at 959 and 948 cm^{-1} , which correspond to the broad band at about 935 cm^{-1} at room temperature are in the

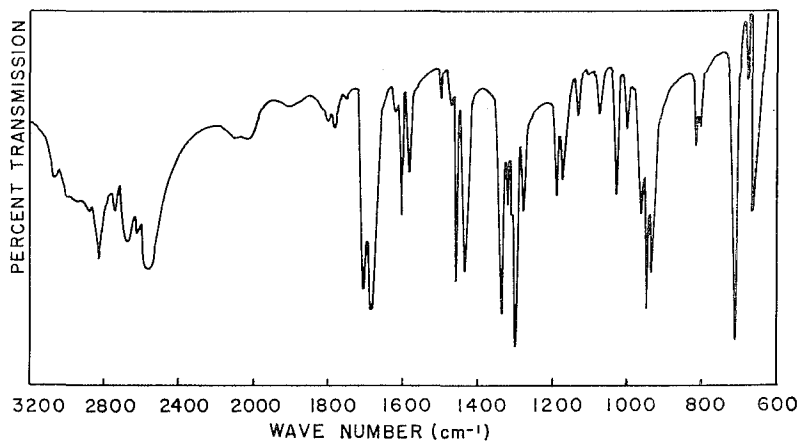


Fig. 2. Infrared spectra of benzoic acid at -150°C .

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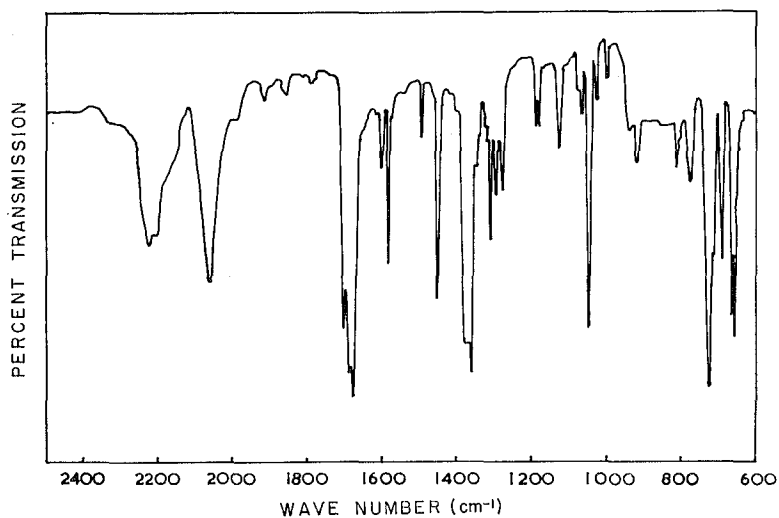


Fig. 3. Infrared spectra of *d*-benzoic acid at -150°C .

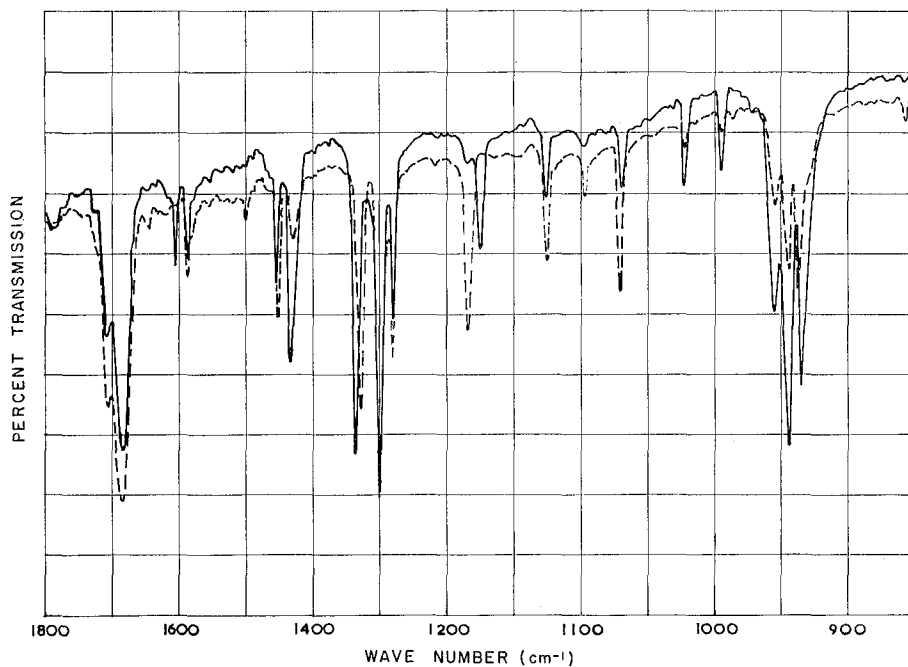


Fig. 4. Polarized infrared spectra of benzoic acid at -150°C .

— *E* vector parallel to *b* axis.

..... *E* vector perpendicular to *b* axis.

region of O—H out-of-plane bending vibration²⁾. These bands disappear on deuteration. The correspondence of the bands between the benzoic and deuterobenzoic acids is given in Table 1, together with assignments of them.

2. Causes of the splitting

Polarized infrared spectra of Figure 4 measured at -150°C show that bands

Table 1. Characteristic Frequencies of Benzoic and Deuterobenzoic Acids.
at -150°C

$(\text{RCOOH})_2$			$(\text{RCOOD})_2$		
Frequency cm^{-1}		Configurations and assignments**	Frequency cm^{-1}		Configurations and assignments
1706	A	$\nu \text{ C}=\text{O}$	1700	A	$\nu \text{ C}=\text{O}$
1684	B		1684	B	
			1674		
1432		$\nu \text{ C}-\text{O}+\delta \text{ OH}$	1375*		$\nu \text{ C}-\text{O}$
			1350		
1334	B	$\delta \text{ OH}+\nu \text{ C}-\text{O}$	1321*		B $\delta \text{ OD}$
1298	A		1293*		
			1064	B	
			1044	A	
959	B	$\sigma \text{ OH}$ due to benzene ring	930*		A $\sigma \text{ OH}+\text{benzene ring}$
948	A		917*		
			730*		
707			718*		
			725	A	B $\sigma \text{ OH}$
			710	B	
			690	A	
808		$\nu \text{ C}-\text{C}$	783	B	$\nu \text{ C}-\text{C}$
			778	A	
684	B	$-\text{C} \begin{smallmatrix} \text{O} \\ \diagup \end{smallmatrix} \text{O}$ scissoring ⁵⁾	668	B	$-\text{C} \begin{smallmatrix} \text{O} \\ \diagup \end{smallmatrix} \text{O}$ scissoring ⁵⁾
670	A		654	A	
554	B	$-\text{C} \begin{smallmatrix} \text{C} \\ \diagup \end{smallmatrix} \text{O}$ scissoring ⁵⁾	546	B	$-\text{C} \begin{smallmatrix} \text{C} \\ \diagup \end{smallmatrix} \text{O}$ scissoring ⁵⁾
543	A		536	A	

* Bands perhaps due to $\text{RCOOH} \cdot \text{RCOOD}$ dimers.** ν =stretching; δ =inplane bending; σ =out-of-plane bending

at 1184 and 1174 cm^{-1} have high dichroic ratios. This means that the orientation of samples is good. Hence, the splitting of the bands of low dichroic ratios at 1706 and 1684 cm^{-1} must not be due to the "factor group splitting", caused by the interaction with neighbouring molecules of the crystal. A pair of bands at 1334 and 1298 cm^{-1} as well as the doublet at 959 and 948 cm^{-1} must not be due to the "factor group splitting" either. Moreover, it is difficult to consider that many pairs of the bands are caused by the "Fermi resonance". Another type of explanation³⁾ of the splitting of bands of the carboxylic group is the tunnelling motion of hydrogen atoms in the O—H groups of the acid dimers from one equiva-

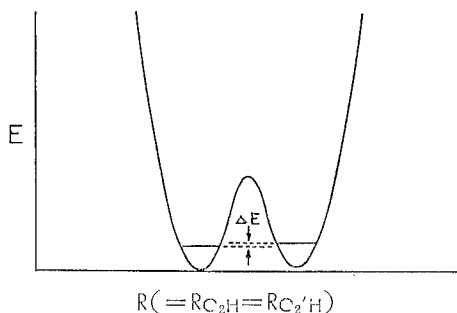


Fig. 5. Asymmetric double minimum potential.

lent position to another. Although such a phenomenon would give rise to the splitting of the Raman-active $\nu\text{O—H}$ energy levels into pairs⁴¹, infrared-active bands of $\nu\text{C=O}$, $\nu\text{C—O} + \delta\text{OH}$ and σOH would be difficult to give rise to the splitting by tunnelling effect.

Consequently, we consider that the two configurations of Figure 1(A) and (B) with different energies and different spectra exist in the crystal. Figure 5 shows the potential energy curve of the dimer in the crystal. The two potential minima would be different from each other. The lower and higher potential minima correspond to the configurations A and B of Figure 1, respectively.

3. Energy difference

If the two configurations exist and the ratio of absorption coefficients of a pair is constant, the energy difference (ΔE_0) between configurations A and B can be obtained by measuring intensity ratios of the pair at various temperatures from

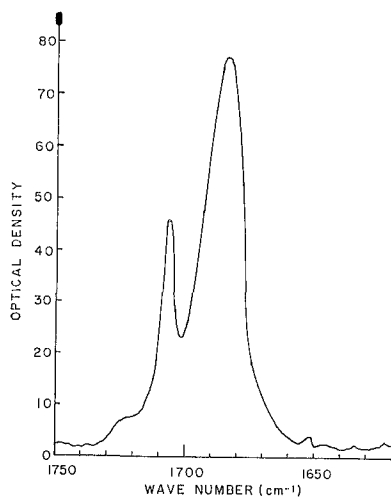


Fig. 6(a). C=O bands at -160°C .

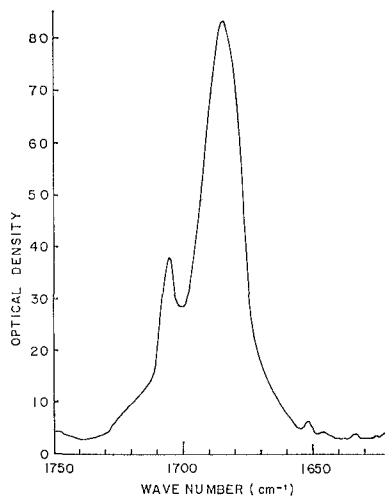


Fig. 6(b). C=O bands at -80°C .

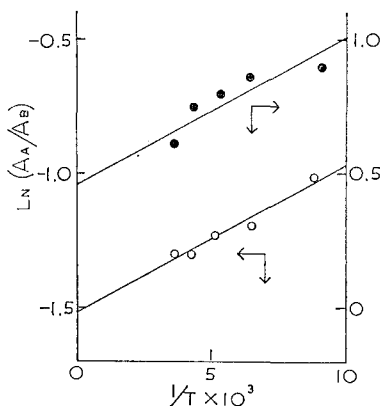


Fig. 7. Temperature dependences of band areas of pairs.

—●—●— A pair at *ca.* 1300 cm^{-1} .
—○—○— A pair at *ca.* 1700 cm^{-1} .

the following equation:

$$\ln \frac{A_A}{A_B} = \ln \left(\frac{K_B}{K_A} \cdot e^{\Delta S/R} \right) - \frac{\Delta E}{RT}, \quad (1)$$

where A_A and A_B are the band areas for absorption assigned to the configurations A and B respectively, K_A and K_B the absorption coefficients of corresponding bands, and ΔS and ΔE the differences of entropy and enthalpy between the configurations A and B, respectively. Figure 6 shows the pair of bands due to C=O stretching vibration at various temperatures. From the linearity of $\ln(A_A/A_B)$ against $1/T$, shown in Figure 7, the energy difference is estimated to be about 0.1 Kcal./mole.

4. Interpretation for nearly equal C—O distances

The C—O distances of gaseous dimers of formic and acetic acids have been determined by using the electron diffraction⁶⁾. The longer and shorter values for these acids are 1.36 and 1.25Å, and those for nicotinic acid are 1.18 and 1.34Å, respectively. The differences of these distances are larger than those for the benzoic acid. The nearly equal C—O distances for the benzoic acid, *i.e.* 1.29 and 1.24Å, may be interpreted as averages for the mixture of the two configurations with a larger difference in C—O distances than that actually observed.

ACKNOWLEDGMENT

The authors wish to thank Professor R. Gotoh for his kind advices and encouragement throughout this work.

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